



## Fabrication of large-area multi-element two-dimensional materials

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(57) Abstract: The present invention relates to a method for fabri-  
cating large-area, monolayer sheets of a multi-elemental two-dimen-  
sional material having the general formula  $M_mX_n$ .

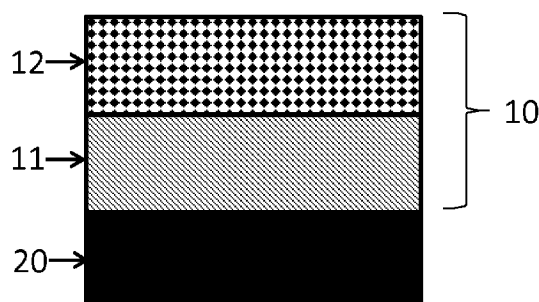


Fig. 1A

## FABRICATION OF LARGE-AREA MULTI-ELEMENT TWO-DIMENSIONAL MATERIALS

## TECHNICAL FIELD

The present invention relates to a method for fabricating large-area, monolayer sheets of a multi-elemental two-dimensional material.

## 5 BACKGROUND

Two-dimensional (2D) materials have seen an exponential rise in interest from industry and academia in recent years due to their unique electronic and optical properties and the possibility of fabricating complex, tailor-made three-dimensional (3D) crystals from them. To date, almost 2500 two-dimensional materials have been identified; such a large library of materials gives great flexibility in finding a material with the exact set of properties one desires; moreover, stacking these materials into 3D 'van-der-Waals (vdW) heterostructures' results in a synergistic combination of their properties in the resulting crystal. For instance, highly efficient solar cells have been demonstrated by making vdW heterostructures out of different semiconducting 2D materials with different optical band gaps. The ability to fabricate tailor-made vdW heterostructures is thus expected to lead to major breakthroughs in the fields of optoelectronics, photovoltaics, flexible displays and electronics, and catalysis.

Only a few of the vast range of potential two-dimensional materials have been isolated or synthesised to date. Typically, 2D materials are discovered by mechanically exfoliating naturally occurring bulk crystals to produce atomically thin layers, after which a material-specific vapour synthesis method must be developed to grow interesting candidates in a scalable manner.

A large number of 2D materials are binary compounds with the designation  $MX_n$ , where M is typically a transition metal and X a chalcogen or non-metal from groups IV, V, and VI. The molybdenum and tungsten disulphides and diselenides remain the most commonly studied 2D binary compounds, with the notable exception of hexagonal boron nitride (hBN) - due to the ready availability of naturally occurring bulk crystals amenable to exfoliation. Chemical vapour deposition (CVD) techniques for the scalable synthesis of these materials are available. However, controlling the stoichiometry and hence the defect density can be challenging. Such techniques typically employ solid metal oxide or metal-organic precursors which are chalcogenated at elevated temperatures. Finding appropriate metal precursors is often a limiting challenge for extending these methods to other 2D transition metal

compounds, and the methods typically require dedicated processes and equipment that are highly optimised for growing one specific material.

A major obstacle facing the field, however, is that there currently exists no generic method for fabricating monolayers of these materials of (1) a given elemental composition and (2) on a large scale. The method described herein, is believed to be sufficiently robust so as enable industrial-scale production of two-dimensional materials.

C. Xu, et al., *Nature Materials* 4374, 2015 08 17 describes the growth of 2D  $\alpha$ -Mo<sub>2</sub>C crystals in a chemical vapour deposition (CVD) process, with methane (gas) as the carbon source. The gas is applied to a Cu foil which is sitting on a Mo (metal) foil.

Other references in this field of research include Yang Gao, et al., *Nature Communications* 9569, 2015 10 09 and US 9359211.

## SUMMARY

A general approach for synthesising thin layers of two-dimensional binary compounds from elemental solid metal precursors is presented. Published CVD growth models for binary compounds stipulate that both elements be insoluble in the catalyst to ensure surface-limited growth, by analogy with CVD graphene growth on copper. In fact, only one component of a binary compound need be insoluble to achieve surface-limited growth, as demonstrated by Kidambi, P. R. et al in "In-situ observations during chemical vapour deposition of hexagonal boron nitride on polycrystalline copper". *Chem. Mater.* 26, 6380–6392 (2014). Here, monoatomic layers are grown despite the solubility of boron in copper. The growth of 26 materials is shown, including transition metal sulphides, selenides, tellurides, and nitrides. A method described further below is used to synthesize a range of atomically thin binary compounds which, due to the lack of a layered bulk crystal amenable to exfoliation, have never been isolated or studied before. This approach greatly simplifies the synthesis of currently known materials, and provides a general framework for synthesising both predicted and unexpected new 2D compounds.

A method is provided for forming a two-dimensional monolayer having the general formula  $M_mX_n$  in which M is selected from: at least one semi-metal or metal from groups 13, 14, 15, or 16; at least one transition metal; at least one a metal from groups 1 or 2; or combinations thereof; and in which X is at least one non-metal or semi-metal, and wherein  $m$  and  $n$  are rational numbers greater than 0; said method comprising the steps of:

- a. providing a solid phase layer comprising said at least one component M and a gold catalyst; and
- b. exposing the solid phase layer to a gas phase under controlled temperature and pressure (i.e. under CVD conditions), the gas phase comprising said at least one non-metal or semi-metal X; wherein X has substantially no solubility in the solid phase, and the gas phase has substantially no solubility in the solid phase layer;

such that a two-dimensional monolayer between M and X is formed on the surface of said solid phase layer, and at the interface of said solid phase layer and gas phase.

- 10 In the described method, the use of a gold catalyst is a critical step for achieving surface-limited conditions for growing arbitrary 2D  $M_nX_n$  compounds. Gold readily alloys with most transition metals M, but shows limited solubility for X elements at our growth temperatures. Moreover, gold is unique in that it does not react with X precursors at these temperatures. Finally, gold is catalytically active, which aids in the formation of crystalline atomically thin materials.

The formation of 2D monolayers is dominated by precipitation of component M from the catalyst bulk upon reacting with X at the solid-gas interface at the surface of the catalyst. The crucial point is that surface-limited growth does not require the metal precursor to be insoluble in the catalyst layer. This fact allows the method to be applicable to all precursor metals.

#### LEGENDS TO THE FIGURES

Figure 1A schematically illustrates a solid phase layer (10) comprising said at least one component M and a gold catalyst on at least one surface of a support substrate (20). In this figure, the solid phase layer (10) comprises one sub-layer (11) of said at least one component M and at least one sub-layer of said gold catalyst (12). In this Figure, the sub-layer of said at least one component M (11) is arranged adjacent the support substrate (20).

Figure 1B schematically illustrates a solid phase layer (10) comprising said at least one component M and a gold catalyst on at least one surface of a support substrate (20). In this figure, the solid phase layer (10) comprises one sub-layer (11) of said at least one component M and two sub-layers (12) of said gold catalyst, wherein the metal/semi-metal sub-layer is arranged between said gold sub-layers.

Figure 1C schematically illustrates a solid phase layer (10) comprising said at least one component M and a gold catalyst on at least one surface of a support substrate (20). In this figure, the solid phase layer (10) comprises a mixed layer of co-deposited at least one component M and gold catalyst.

Figure 1D schematically illustrates a solid phase layer (10) comprising said at least one component M and a gold catalyst on at least one surface of a support substrate (20). In this figure, the solid phase layer (10) comprises one sub-layer (11) of said at least one component M and at least one sub-layer of said gold catalyst (12). In this figure, the sub-layer of gold catalyst (12) is arranged adjacent the support substrate (20).

Figure 2 shows the results of applying the same growth conditions to various combinations of M (Mo, W, Cr, Fe, Co, Hf, Nb, Pd, Pt, V, Ta) and X (S, Se, Te) so as to produce a range of transition metal chalcogenides, some of which have not been previously synthesized or isolated as atomically thin layers, or whose layered phases are not easily accessible as bulk exfoliable crystals (e.g. the Cr, Fe and Co chalcogenides). Figures 2A-2C are scanning electron micrographs (SEM) of various monolayers created via the general method described herein. All presented materials are grown under identical process conditions, varying only M and X. Scale bars are 1  $\mu\text{m}$  except where marked: \*: 100 nm, \*\*: 10  $\mu\text{m}$ . Figure 2A illustrates 24 different monolayers: monolayer triangles of molybdenum, disulphide  $\text{MoS}_2$ ,  $\text{MoSe}_2$ ,  $\text{MoTe}_2$ , monolayer triangles of tungsten, disulphide  $\text{WS}_2$ ,  $\text{WSe}_2$ ,  $\text{WTe}_2$ , monolayers of chromium,  $\text{CrS}_2$ ,  $\text{CrSe}_2$ ,  $\text{CrTe}_2$ , monolayers of iron,  $\text{FeS}$ ,  $\text{FeSe}$ ,  $\text{FeTe}$ , monolayers of cobalt,  $\text{CoS}_2$ ,  $\text{CoSe}_2$ ,  $\text{CoTe}_2$ , hafnium sulphide,  $\text{HfS}_2$ , a monolayer niobium disulphide,  $\text{NbS}_2$ , having triangular morphology,  $\text{PdS}_2$ ,  $\text{PtS}_2$ , vanadium disulphide,  $\text{VS}_2$ , also having a triangular morphology, tantalum disulphide,  $\text{TaS}_2$ , with a triangular morphology as well  $\text{PtSe}_2$ ,  $\text{VSe}_2$ , and  $\text{TaSe}_2$ .; Figure 2B is tin disulphide,  $\text{SnS}_2$ , with a triangular morphology; Figure 2C shows atomically thin niobium oxynitride,  $\text{Nb}_x\text{O}_y\text{N}_z$ .  $\text{Nb}_x\text{O}_y\text{N}_z$  is a new two-dimensional material. The presented materials display a range of morphological tendencies. Except for the iron-group metals (Co, Fe), they form few-atom thick layers: the iron-group metals display both thin layers and monolithic layered structures.  $\text{PtS}_2$  and  $\text{PtSe}_2$  both show circular domains rather than the hexagonal or faceted structures expected for platinum chalcogenides. In control experiments performed without exposure to X vapour, similar circular domains are observed. Substituting ammonia vapour for X provides a source of nitrogen for the growth of previously unreported transition metal nitrides.

Figure 3 is a schematic representation of the apparatus 300 used in the synthesis of 2D monolayer materials. The solid phase layer 301, possibly placed on a substrate, is placed inside the furnace 302, and heated to reaction temperature  $T_2$ , (between  $700^\circ\text{C}$  -  $1000^\circ\text{C}$ ) and is annealed at this temperature for 1 hour. A gas is flowed into the chamber 303

throughout the process. The arrow 304 indicates gas flow through the chamber 303. To initiate the growth process, solid powder/flakes 305 loaded upstream to the solid phase layer 301 are heated inside the heating belt 306 to a precursor temperature  $T_1$  (between 100°C - 150°C to generate a vapour. This vapour is then transported into the furnace 302 by the gas flow, where it comes into contact with the solid phase layer 301 and reacts to form a monolayer. After the growth process is carried out, both the furnace 302 and heating belt 306 are shut off.

#### DETAILED DISCLOSURE

Binary elemental materials are generally ascribed the formula 'MX', where M represents one component, usually a metal, and X represents a second, different component, usually from the groups 13, 14, 15, or 16 of the periodic table. The present method exploits the mutual insolubility of the two components in different phases to limit the interaction between the components at the interface of the aforementioned phases. For instance, component M exists in a solid phase 1, and component X exists in the gas phase 2; a key aspect of the invention is that component M has limited or no solubility in phase 2, and that component X has limited or no solubility in phase 1. In the present context, a two-dimensional monolayer refers to a material which is either 1-atomic layer thin or comprises a thickness corresponding to 1 atomic layer of the material.

A method is provided for forming a two-dimensional monolayer having the general formula  $M_mX_n$ .

M is at least one semi-metal and/or metal from groups 13, 14, 15, or 16, and/or a transition metal from groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and/or 12, and/or a metal from groups 1 or 2, preferably groups 4, 5 or 6. Preferably, only one component M is present in the monolayer. In one aspect, component M is selected from Hf, Zr, Ti, Nb, Ta, V, Mo, W, Cr, Ni, Co, Re, Pt, Pd, Ga, In, Sn, Ge, and Bi, preferably Mo, Cr, Fe, Co, Pt, V, Ta or W.

X is at least one non-metal or semi-metal. X is suitably selected from groups 13, 14, 15, or 16 of the periodic table, most suitably from groups 14, 15 or 16. In one aspect, component X may be selected from the group consisting of S, Se, Te, O, C, N, P, Si and As, preferably S, Se or N, more preferably S, Te or Se. Preferably, only one component X is present in the monolayer.

In the general formula  $M_mX_n$ , m and n are rational numbers greater than 0. Namely, m and n can be fractions, especially when M or X comprises more than one component, and one or

more of those components act as a dopant. Suitably, both  $m$  and  $n$  are 1 or 2; most suitably,  $m$  is 1 while  $n$  is 1 or 2; i.e. the monolayer has the general formula MX or MX<sub>2</sub>.

The first step of the general method comprises: providing a solid phase layer. The solid phase layer comprises said at least one component M and a gold (Au) catalyst. The solid phase layer is commonly provided on at least one surface of a support substrate.

Gold is the most favourable metal for use here as it readily forms alloys with most of the metals/semi-metals M in the periodic table, but has limited solubility for most of the X components at temperatures favourable for MX synthesis. Furthermore, it is a highly inert metal that does not itself react with the components participating in the reactions. It mainly participates in the reactions only as a catalyst.

As shown in the embodiments on Figures 1A-1B, the solid phase layer comprises at least one sub-layer (11) of said at least one component M and at least one sub-layer (12) of said gold catalyst. In figure 1A – the most common arrangement – the solid phase layer (10) comprises one sub-layer (11) of said at least one component M and at least one sub-layer of said gold catalyst (12). In this figure, the sub-layer of component M (11) is arranged adjacent the support substrate (20).

In Figure 1B, the solid phase layer (10) comprises one sub-layer (11) of said at least one component M and two sub-layers (12) of said gold catalyst, and the metal/semi-metal sub-layer (11) is arranged between said gold sub-layers.

The at least one metal/semi-metal sub-layer (11) may comprise a plurality of metals/semi-metals (M1, M2, M3...), wherein said plurality of metals/semi-metals (M1, M2, M3...) are arranged as separate layers within said metal/semi-metal sub-layer (11), or are a mixture of co-deposited metals/semi-metals (M1, M2, M3...) in the same sub-layer (11).

The typical thickness of the gold sub-layer (12) is above 100 nm, such as above 200 nm.

Each metal/semi-metal sub-layer (11) has a typical thickness that would comprise no more than 50% (the atomic percent) of the gold layer, such as less than 40%, such as less than 30%, such as less than 15%, such as less than 5%. Exceptions are metals which do not significantly dissolve in gold or form intermetallic phases such as Mo and W. For those, the thickness of the metal layer and gold layer can be arbitrary.

In Figure 1C the solid phase layer (10) comprises a mixed layer of co-deposited at least one component M and gold catalyst. The quantity of component M in the solid phase layer may



comprise no more than 50% (the atomic percent) of the quantity of the gold in the layer, such as less than 40%, such as less than 30%, such as less than 15%, such as less than 5%.

In Figure 1D the solid phase layer (10) comprises one sub-layer (11) of said at least one component M and at least one sub-layer of said gold catalyst (12). Compared to Figure 1A, the sub-layer of gold catalyst (12) is arranged adjacent to the support structure (20). At least one component M is deposited on the gold catalyst (12) and then annealed. Later on, in the second step, annealed solid phase is exposed to a gas phase comprising at least one component X. The gold layer (12) plays a catalytic role, and monolayer growth is achieved by exploiting the insolubility of component X in the gold layer (12).

- 10 The layers and sub-layers of at least one component M can be formed as required, using e.g. sputter coating, evaporation, electroplating, direct fusion of two metal foils, or any other known metal/semi-metal deposition technique.

Suitably, the solid phase layer is provided by co-deposition or sequential deposition of said at least one component M and a gold catalyst from elemental vapor form or aqueous solution.

- 15 By the term "elemental vapor form" is meant that neither the component M nor the gold catalyst are chemically bonded to any other element in this vapor form.

The solid phase layer is a "bulk alloy" between component M and the gold.

- 20 In the second step of the general method, the solid phase layer is exposed under CVD conditions to a gas phase comprising said at least one component X; wherein X has substantially no solubility in the solid phase, and the gas phase has substantially no solubility in the solid phase layer. CVD is a deposition process wherein volatile precursors are introduced into a reaction chamber containing a target substrate, usually in solid form, under controlled temperature and pressure conditions. The precursors adsorb onto the substrate surface, where they decompose and/or react to form the desired material. CVD is desirable over other processes for thin film deposition (e.g. – physical vapour deposition (PVD), reactive PVD, etc.) because it is simple and can operate over a wide range of temperatures and pressures, making it more industrially scalable, and results in higher quality films for multi-elemental compounds.

- 30 In one embodiment of the method, the component M diffuses into the gold catalyst, and a diffusion gradient therefore exists within the solid phase layer or the gold sub-layer, with a decrease in the metal/semi-metal content towards the surface of the solid phase layer. As a result of this dissolution profile, the interaction between M and X atoms can only take place at the surface where the atoms X are localized, thereby localizing the components at this

two-dimensional interface between the phases and guaranteeing surface-limited growth of monolayer films of MX. A two-dimensional monolayer between M and X is thus formed on the surface of said solid phase layer and at the interface of said solid phase layer and gas phase.

The most direct implementation of the method employs a solid phase 1 and a gaseous phase 2, with the component M being pre-dissolved in the solid phase as a metal/semi-metal alloy or as an intermetallic compound, and component X being introduced either as a gaseous precursor in phase 2 or as a volatile vapour in the same.

The gas phase may consist of a gaseous precursor to said component X or a volatile vapour of said component X. In one aspect, the gas phase consists of said at least one component X and a carrier gas such as Ar or H<sub>2</sub> or N<sub>2</sub> which comprises the majority of the volume of the gas flow. As above, the component X may be selected from the group consisting of S, Se, Te, O, C, N, P, Si and As, preferably S, Se or N. In the gas phase, component X may be in the form of a hydride of said component, e.g. CH<sub>4</sub>, H<sub>2</sub>S, NH<sub>3</sub>, or PH<sub>3</sub>.

In the method according to the invention, the % atomic composition of the at least one component M in the gold layer is suitably less than 50%, such as less than 25%, and preferably less than 10%.

In the method according to the invention, the support substrate is suitably selected from the group consisting of sapphire, glass, alumina or metallic gold. In embodiments in which there is no support substrate as such, the component M layer serves as a support. An example may be a tungsten foil coated with a thin film of gold. Additionally, if the method is to be scaled for roll-to-roll production, a special support that offers flexibility and can withstand high temperatures can be engineered. An example may be an Mo or other metallic foil that is sputter-coated or atomic layer deposition (ALD) coated with a diffusion barrier such as a nitride, and finally coated with gold and component M. The support substrate may not contaminate the gold layer with other compounds/metals.

The method of the invention allows the synthesis of new 2D monolayer materials which have not previously been known. 2D monolayers which can be synthesised by the method of the invention include those with a formula selected from the group consisting of TaN, NbN, NbS<sub>2</sub>, TaS<sub>2</sub>, SnS<sub>2</sub>, HfS<sub>2</sub>, MoSe<sub>2</sub>, MoTe<sub>2</sub>, WSe<sub>2</sub>, WTe<sub>2</sub>, CrS<sub>2</sub>, CrSe<sub>2</sub>, CrTe<sub>2</sub>, FeS, FeSe, FeTe, CoS<sub>2</sub>, CoSe<sub>2</sub>, CoTe<sub>2</sub>, PdS<sub>2</sub>, PtS<sub>2</sub>, PtSe<sub>2</sub>, VS<sub>2</sub>, and TaSe<sub>2</sub>.

Typically, a thin layer of approximately 20 nm of metal layer M is sputtered onto c-plane sapphire and encapsulated by a thick layer (~500 nm) of gold. Namely, substrates are prepared by physical vapour deposition of a thin layer (~20 nm) of metal M followed by a

thick layer (between 300 nm – 1  $\mu$ m, typically  $\sim$ 500 nm) of gold (Lesker, 99,999%) on a <001> sapphire substrate. Oxidation of the metal M is avoided by immediate encapsulation with gold before exposure to ambient conditions. The M-Au layer is then heated to 850°C to form an alloy. The relative thicknesses of the M and Au layers determines the concentration of M in the final alloy, which here is deliberately limited to  $\leq$  5 at% in order to maintain single-phase alloying conditions. The Au-M alloy is subsequently exposed to a vapour-phase precursor of component X. The limited solubility of X in the gold restricts the formation of MX<sub>n</sub> compounds to the surface of the alloy, resulting in few-atom thick layers of binary compounds.

## 10 EXAMPLES

### 1. Synthesis of Metal sulphides:

The experimental schematic in Figure 3 shows the experimental setup that can be used to grow 2D metal sulphides.

The solid phase layer plus substrate is placed inside a furnace and heated to reaction temperature (between 700°C -1000°C) and is annealed at this temperature for 1 hour. T<sub>1</sub> and T<sub>2</sub> refer to the precursor and furnace temperatures, respectively. 100 sccm Ar is flowed into the chamber throughout the process, and the chamber pressure is maintained at 1.2 Torr. To initiate the growth process, sulphur powder/flakes loaded upstream to the substrate are heated to 100°C -150°C to generate sulphur vapour (the sulphur vapour pressure becomes significant when it approaches/crosses its melting point of 115°C). This vapour is then transported into the reaction chamber by the argon gas flow, where it comes into contact with the substrate and reacts to form monolayer metal sulphides. The growth process is carried out for 30 minutes, after which the growth is terminated by shutting off both the reactor and heating belt. This embodiment may be applied when a solid precursor is used to generate precursor X in the gas phase. In this embodiment, elemental sulphur vapour is being generated by heating the sulphur.

In this setup, a solid sulphur source was used. However, other sulphur sources can also be used. For example, H<sub>2</sub>S gas can be used. In this case, the H<sub>2</sub>S gas can either be generated by introducing H<sub>2</sub> gas while the sulphur is being heated, or it can be fed in gas form into the furnace. The argon serves as a carrier gas for the sulphur, but N<sub>2</sub> can also be used. Moreover, H<sub>2</sub> can also be added (in fact, it may be needed for high quality growths) as a carrier gas.

Using this setup, MoS<sub>2</sub> and WS<sub>2</sub>, can for instance be grown. The gold catalyst typically adopts an Au {111} surface on the {001} sapphire substrate, leading to epitaxial growth of the dichalcogenide layers, with domain sizes on the order of 100 µm.

## 2. Synthesis of Metal Selenides:

- 5 The same experimental procedure would be used as for sulphides.

When solid selenium would be used as the source, the T<sub>1</sub> temperature would needed to be increased to 200°C - 300°C to generate enough vapour. H<sub>2</sub>Se can be alternatively used in a similar fashion to sulphide growth.

## 3. Synthesis of Metal Tellurides:

- 10 This synthesis is carried out in a similar fashion to selenides and sulphides, where solid tellurium is heated to near its melting point to generate tellurium vapour. Gaseous tellurium-based compounds can also be alternatively used in a similar fashion to sulphide and selenide growths.

- 15 As tellurium is a semi-metal that can be sputter-coated, one alternative method for fabricating these compounds may be that tellurium thin films are directly sputtered on top of gold/metal alloys, and the sample is subsequently heated to 450°C, whereby surface reaction forms tellurides and the excess tellurium is thermally evaporated simultaneously.

- 20 When creating WTe<sub>2</sub>, Te can act as component M and W can act as component X. W may be introduced as volatilized WO<sub>3</sub> vapours, and Te may be alloyed with gold. This may be a special case for any metal which is not soluble in gold, such as tungsten.

## 4. Synthesis of Nitrides:

The same process applies for nitrides as for sulphides, except that ammonia is used as a nitrogen source. Ammonia is fed in gas form along with argon (and/or hydrogen) carrier gas. The temperature T<sub>1</sub> is maintained at 950°C-1050°C.

## CLAIMS

1. A method for forming a two-dimensional monolayer having the general formula  $M_mX_n$  in which M is selected from: at least one semi-metal or metal from groups 13, 14, 15, or 16; at least one transition metal; at least one a metal from groups 1 or 2; or combinations thereof; and in which X is at least one non-metal or semi-metal, and wherein m and n are rational numbers greater than 0; said method comprising the steps of:

- a. providing a solid phase layer comprising said at least one component M and a gold catalyst; and
- b. exposing the solid phase layer to a gas phase under controlled temperature and pressure conditions, the gas phase comprising said at least one non-metal or semi-metal X; wherein X has substantially no solubility in the solid phase, and the gas phase has substantially no solubility in the solid phase layer;

such that a two-dimensional monolayer between M and X is formed on the surface of said solid phase layer, and at the interface of said solid phase layer and gas phase.

2. The method according to claim 1, wherein the solid phase layer comprises at least one sub-layer of said at least one component M and at least one sub-layer of said gold catalyst.

3. The method according to any one of claims 1-2, wherein the solid phase layer is provided on at least one surface of a support substrate.

4. The method according to any one of claims 2-3, wherein a sub-layer of said at least one component M is arranged adjacent the support substrate.

5. The method according to any one of the preceding claims, wherein the solid phase layer comprises one sub-layer of said at least one component M and two sub-layers of said gold catalyst, wherein the metal/semi-metal sub-layer is arranged between said gold sub-layers.

6. The method according to any one of the preceding claims, wherein said at least one metal/semi-metal sub-layer comprises a plurality of metals/semi-metals (M1, M2, M3...), wherein said plurality of metals/semi-metals (M1, M2, M3...) are arranged as separate layers within said metal/semi-metal sub-layer, or are a mixture of co-deposited metals/semi-metals (M1, M2, M3...) in the same sub-layer.

7. The method according to claim 1, wherein the solid phase layer comprises a mixed layer of co-deposited at least one component M and gold catalyst.

8. The method according to any one of the preceding claims, wherein the gas phase consists of a gaseous precursor to said component X or a volatile vapour of said component X.

9. The method according to any one of the preceding claims, wherein the gas phase consists of said at least one component X.

10. The method according to any one of the preceding claims, wherein the at least one component M is selected from the group consisting of Hf, Zr, Ti, Nb, Ta, V, Mo, W, Cr, Ni, Co, Re, Pt, Pd, Ga, In, Sn, Ge, and Bi, preferably Mo, Cr, Fe, Co, Pt, V, Ta or W.

11. The method according to any one of the preceding claims, wherein M is selected from groups 4, 5, 6, 7, 10, 13, 14, or 15 of the periodic table, preferably groups 5, 6 or 7.

12. The method according to any one of the preceding claims, wherein the component X is selected from the group consisting of S, Se, Te, O, C, N, P, Si and As, preferably S, Se or N, more preferably S, Te or Se.

13. The method according to any one of the preceding claims, wherein the component X is in the form of a hydride of said component, e.g. CH<sub>4</sub>, H<sub>2</sub>S, NH<sub>3</sub> or PH<sub>3</sub>.

14. The method according to any one of the preceding claims, wherein the % atomic composition of the at least one component M in the gold layer is less than 50%, preferably less than 10%.

15. The method according to any one of the preceding claims, wherein the support substrate is selected from the group consisting of sapphire, glass, alumina or metallic gold.

16. The method according to any one of the preceding claims, wherein said solid phase layer is provided by co-deposition or sequential deposition of said at least one component M and a gold catalyst from elemental vapor form or aqueous solution.

17. A two-dimensional monolayer having a formula selected from the group consisting of TaN, NbN, WS<sub>2</sub>, MoS<sub>2</sub>, NbS<sub>2</sub>, TaS<sub>2</sub>, SnS<sub>2</sub>, HfS<sub>2</sub>, MoSe<sub>2</sub>, MoTe<sub>2</sub>, WSe<sub>2</sub>, WTe<sub>2</sub>, CrS<sub>2</sub>, CrSe<sub>2</sub>, CrTe<sub>2</sub>, FeS, FeSe, FeTe, CoS<sub>2</sub>, CoSe<sub>2</sub>, CoTe<sub>2</sub>, PdS<sub>2</sub>, PtS<sub>2</sub>, PtSe<sub>2</sub>, VS<sub>2</sub>, and TaSe<sub>2</sub>.

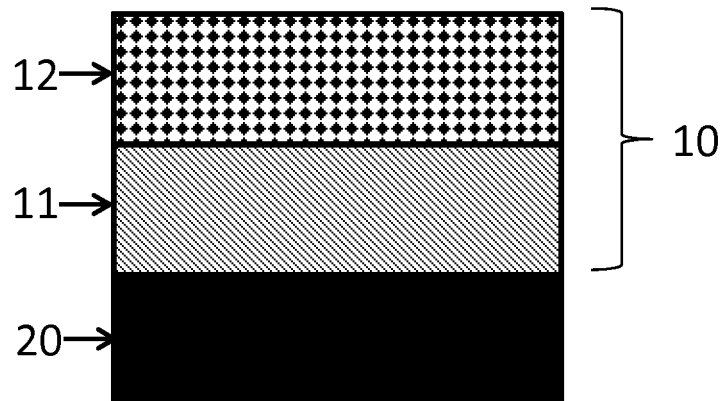


Fig. 1A

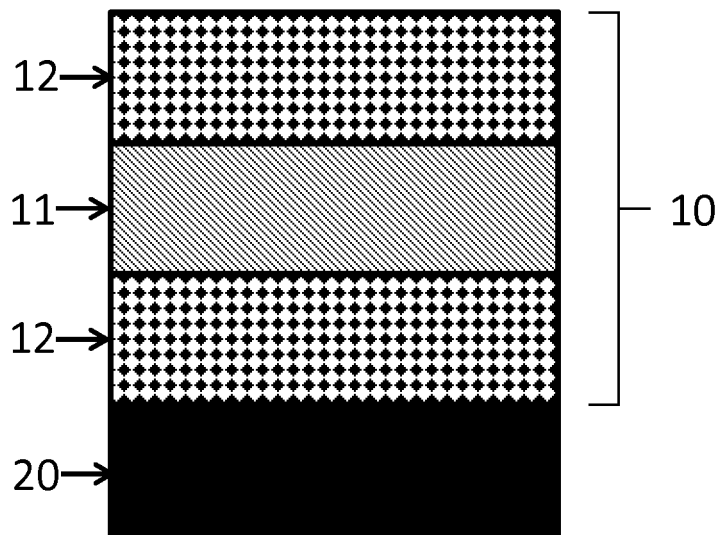


Fig. 1B



Fig. 1C

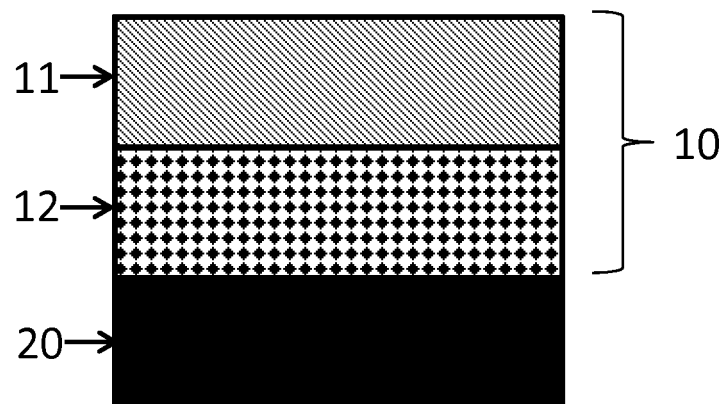


Fig. 1D



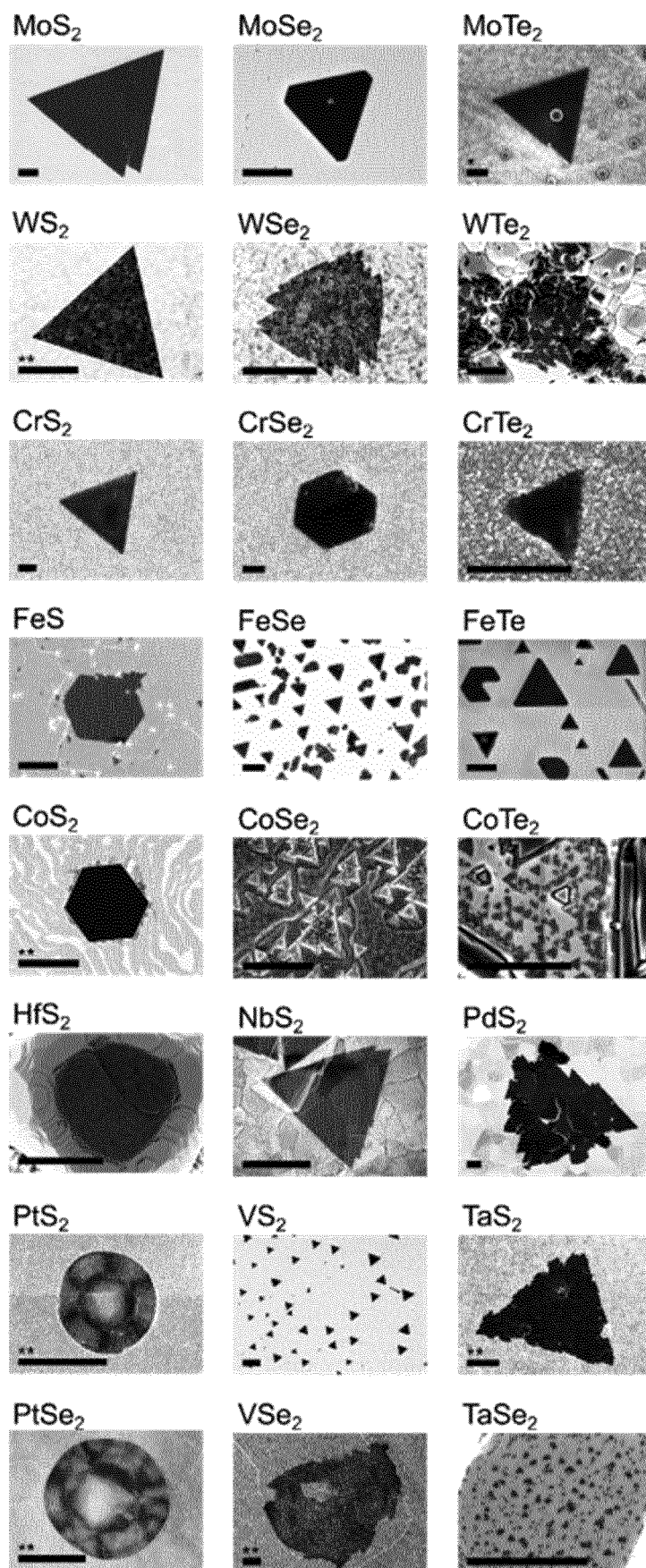


Fig. 2A

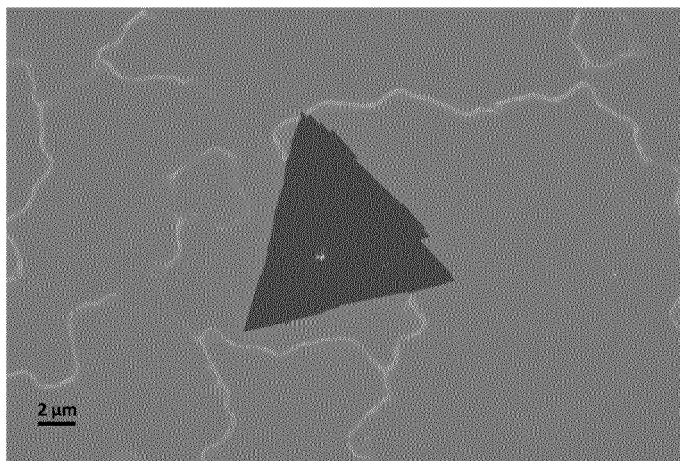


Fig. 2B

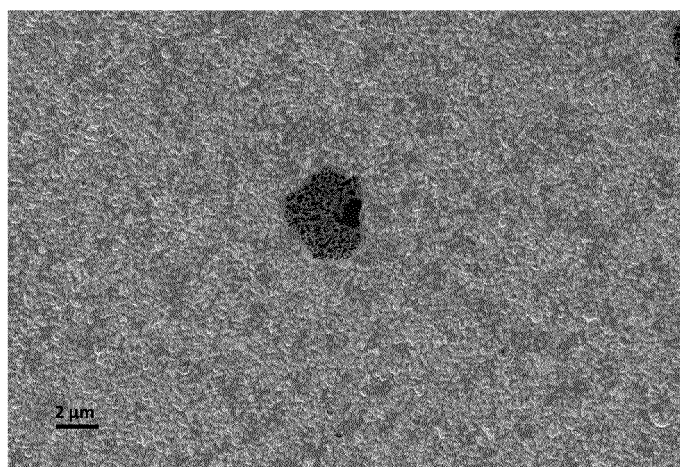


Fig. 2C

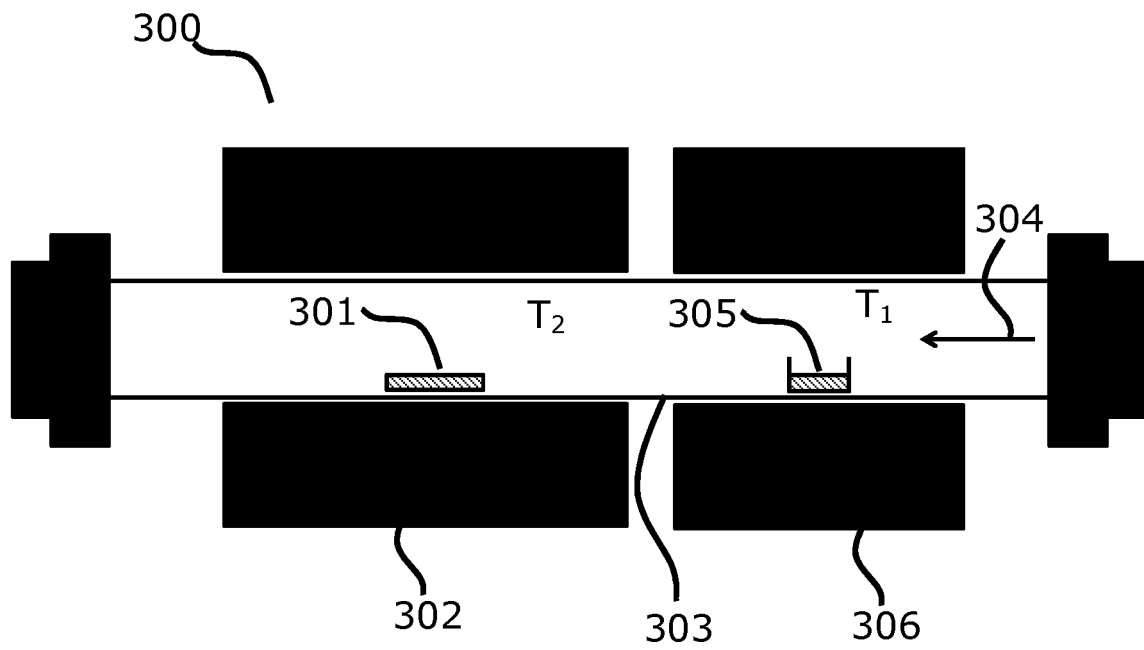


Fig. 3

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/078872

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C30B25/00 C23C14/58 C23C14/14 C23C8/08  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C30B C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>INTEK SONG ET AL: "Patternable Large-Scale Molybdenum Disulfide Atomic Layers Grown by Gold-Assisted Chemical Vapor Deposition", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 53, no. 5, 13 January 2014 (2014-01-13), pages 1266-1269, XP055363756, ISSN: 1433-7851, DOI: 10.1002/anie.201309474 page 1268, right-hand column, paragraph 4 - page 1269, left-hand column, paragraph 2 ----- -/-</p>	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

25 January 2018

Date of mailing of the international search report

20/04/2018

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
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Authorized officer

Schuhmacher, Jörg

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/078872

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SEOK JOON YUN ET AL: "Synthesis of Centimeter-Scale Monolayer Tungsten Disulfide Film on Gold Foils", ACS NANO, vol. 9, no. 5, 26 May 2015 (2015-05-26), pages 5510-5519, XP055363658, US ISSN: 1936-0851, DOI: 10.1021/acsnano.5b01529 page 5517, left-hand column, paragraph 3 -----	17
X	YUN SEOK JOON ET AL: "A systematic study of the synthesis of monolayer tungsten diselenide films on gold foil", CURRENT APPLIED PHYSICS, NORTH-HOLLAND, AMSTERDAM, NL, vol. 16, no. 9, 3 May 2016 (2016-05-03), pages 1216-1222, XP029728682, ISSN: 1567-1739, DOI: 10.1016/J.CAP.2016.02.010 page 1221, left-hand column, paragraph 2 page 1218; figure 2 -----	17
X	YANG GAO ET AL: "Large-area synthesis of high-quality and uniform monolayer WS <sub>2</sub> on reusable Au foils", NATURE COMMUNICATIONS, vol. 6, 9 October 2015 (2015-10-09), page 8569, XP055363866, DOI: 10.1038/ncomms9569 cited in the application page 8, right-hand column, paragraph 2 -----	17
A	CHUAN XU ET AL: "Large-area high-quality 2D ultrathin Mo <sub>2</sub> C superconducting crystals", NATURE MATERIALS, vol. 14, no. 11, 17 August 2015 (2015-08-17), pages 1135-1141, XP055363923, GB ISSN: 1476-1122, DOI: 10.1038/nmat4374 cited in the application page 1140, right-hand column, paragraph 1 -----	13
X	WO 2016/013984 A1 (AGENCY SCIENCE TECH & RES [SG]) 28 January 2016 (2016-01-28) claim 36 ----- -/--	17

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/078872

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>RUDRESH GHOSH ET AL: "Abstract", JOURNAL OF MATERIALS RESEARCH, vol. 31, no. 07, 28 January 2016 (2016-01-28), pages 917-922, XP055443911, US ISSN: 0884-2914, DOI: 10.1557/jmr.2016.7 abstract; figure 1 -----</p>	17

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP2017/078872

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-16(completely); 17(partially)

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-16(completely); 17(partially)

Method of forming a two dimensional monolayer comprising steps a. and b. as indicated in claim 1, characterized by formation of the two-dimensional monolayer on the surface of the solid phase layer comprising gold and metal or semimetal M.

1.1. claim: 17(partially)

Two dimensional monolayer as indicated in claim 17 characterized by having the formula  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{MoSe}_2$  or  $\text{WSe}_2$

---

2. claim: 17(partially)

Two dimensional monolayer as indicated in claim 17 characterized by having the formula  $\text{TaN}$  or  $\text{NbN}$

---

3. claim: 17(partially)

Two dimensional monolayer as indicated in claim 17 characterized by having the formula  $\text{VS}_2$ ,  $\text{NbS}_2$ ,  $\text{TaS}_2$ ,  $\text{TaSe}_2$ , and  $\text{HfS}_2$

---

4. claim: 17(partially)

Two dimensional monolayer as indicated in claim 17 characterized by having the formula  $\text{SnS}_2$

---

5. claim: 17(partially)

Two dimensional monolayer as indicated in claim 17 characterized by having the formula  $\text{MoTe}_2$  or  $\text{WTe}_2$

---

6. claim: 17(partially)

Two dimensional monolayer as indicated in claim 17 characterized by having the formula  $\text{CrS}_2$ ,  $\text{CrSe}_2$  or  $\text{CrTe}_2$

---

7. claim: 17(partially)

Two dimensional monolayer as indicated in claim 17 characterized by having the formula  $\text{FeS}$ ,  $\text{FeSe}$  or  $\text{FeTe}$

---

8. claim: 17(partially)



**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

Two dimensional monolayer as indicated in claim 17  
characterized by having the formula  $\text{CoS}_2$ ,  $\text{CoSe}_2$  or  $\text{CoTe}_2$   
---

9. claim: 17(partially)

Two dimensional monolayer as indicated in claim 17  
characterized by having the formula  $\text{PdS}_2$ ,  $\text{PtS}_2$  or  $\text{PtSe}_2$   
---

## INTERNATIONAL SEARCH REPORT

### Information on patent family members

International application No

PCT/EP2017/078872

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016013984 A1	28-01-2016	SG 11201700604R A	27-02-2017
		US 2017218498 A1	03-08-2017
		WO 2016013984 A1	28-01-2016
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